PATENT SPECIFICATION (11) 1 597 305

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(21) Application No. 21209/78 (22) Filed 22 May 1978 (19)
(31) Convention Application No's 800451 (32) Filed 25 May 1977
895478 11 Apr. 1978 in
(33) United States of America (US)
(44) Complete Specification Published 3 Sep. 1981
(51) INT. CL.^{3} C23F 13/00
(52) Index at Acceptance
C7B 150 509 510 511 512 525

(54) A MARINE POTENTIOMETRIC ANTIFOULING AND ANTICORROSION DEVICE

(71) We, WILLIAM JOSEPH RIFFE, of 609 Bridges Street, Morehead City, North Carolina 28557, United States of America; MARK STAPLETON FOWLER, of 525, North Oxford Street, Arlington, Virginia 22203, United States of America; DAVID MEYERS, of 3428, Gaddy Court, Falls Church, Virginia 22042, United States of America; HARRIS WALLER SEED, of 335, Las Palmas Drive, Santa Barbara, California 93110, United States of America and LOREN ALLAN SMITH, of Yorklyn, Delaware 19736, United States of America, all citizens of the United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The present invention relates to an article having a conductive surface, such as the hull of a ship, provided with an antifouling and anticorrosion device which applies a high voltage potential between a titanium anode and the conductive surface of the article. The high voltage and the small current in the ship's submerged hull surface effectively prevent adherence of marine organisms to the hull while simultaneously preventing corrosion of the hull.

The shipping industry has long faced a serious problem caused by the adherence of marine organisms to ship hulls. Such fouling of a ship's hull increases the operating cost of a ship and decreases its efficiency. Marine organisms which become attached to the hull must periodically be removed, thereby usually taking the ship out of operation for extended periods of time for dry dock maintenance. Also if fouling is not prevented, sea organisms will continue to attach to the hull and will cause ever increasing operating costs associated with additional fuel requirements and decreased speeds.

The prior art teaches several ways of removing marine organisms, including barnacle growth, from a ship. Barnacles can be mechanically scraped from the ship while in dry dock. Cleaning machines have been developed having rotating brushes which can remove barnacles and other marine organisms from the hull.

Another method of overcoming the fouling problem has been to use highly toxic paints on the hulls of ships. Such paints retard the build up of marine growth on the hull. A toxic element in the paint, such as a compound of copper or mercury which is soluble in sea water, is controllably dissolved into the water to provide protection over several years. For example U.S. Patent No. 3,817,759 contemplates the use of an antifouling coating comprising a polymeric titanium ester of an aliphatic alcohol since titanium is known to have good corrosion resistance and low water solubility which prevents premature leaching and exhaustion of the coating.

Another antifouling method described in the prior art has been to coat the hull with a metallic paint whose ions are toxic to marine life, i.e., copper, mercury, silver, tin, arsenic and cadmium, and then to periodically apply a voltage to the hull forcing the toxic ions into solution and thereby inhibiting marine life growth. This method is taught in U.S. Patent No. 3,661,742.

Various other apparatus have been proposed which rely upon application of a voltage to the hull of the ship or provision for flow of current through the hull of the ship to retard growth of marine organisms on the hull. Some systems have proposed the electro-chemical decomposition of sea water causing gases to be produced near the submerged surfaces of the hull. Proponents of such systems maintain that the gases prevent the adherences of marine organisms such as barnacles, algae etc. Others suggest

that high current can cause shock and retard the growth of marine organisms on the hull. None of these systems, however, have proven commercially successful for reasons of cost and poor antifouling results.

Solution to the problem of fouling requires a full understanding of the phenomenon involved. Fouling occurs especially on stationary structures and on ships in port, and there is relatively little fouling of a ship's hull while underway in the open sea. Although not understood in all respects, the phenomenon of fouling apparently is encouraged by bacteria and colloidal particles which in water solution possess an electric charge. For instance, amino acids are negatively charged and in combination as protein molecules are attracted to a ship's hull which is normally positive with respect to the protein molecules. These materials provide the elements of the marine organism food chain and form the initial film which appears on a ship's hull and attracts further sea creatures.

After formation of the initial phase of the food chain on the ship's hull, bacteria will form on the hull surface in one to three days, followed by an algal slime in three to seven days. Protozoans are then formed in one to three weeks and finally barnacles attach to the hull in three to ten weeks. Interruption of the food chain will prevent adherence of marine organisms such as barnacles.

Another problem which in some respects is related to fouling of a ship's hull which the shipping industry has long attempted to solve is that of corrosion. Corrosion normally occurs to underwater portions of a ship's hull because the sea water acts as an electrolyte and current will consequently flow, as in a battery, between surface areas of differing electrical potential. The flow of current takes with it metal ions thereby gradually corroding anodic portions of the hull.

Various techniques have been developed to prevent corrosion. Sacrificial anodes of active metals such as zinc or magnesium have been fastened to the hull. Such anodes, through galvanic action, themselves corrode away instead of the hull. Other systems use cathodic protection by impressed current. Such systems utilize long life anodes which are attached to the hull to impress a current flow in the hull. The result is that the entire hull is made cathodic relative to the anode, thereby shielding it from corrosion. Such systems operate at very low voltage levels.

One cathodic protection system found in the prior art utilizes a titanium anode plated with platinum. The platinum acts as the electrical discharge surface for the anode into the electrolytic sea water. No current is discharged from any surface portions of the electrode comprising titanium. This particular system impresses high current densities on the anode on the order of 550 amps per square foot. Since there is a high current flow from the platinum or other non-soluble anode metal, there is a very low potential. There is essentially no current flow from the surface of the titanium. An example of such a system is disclosed in U.S. Patent No. 3,313,721.

A titanium alloy has in another prior art system been used as a sacrificial anode. A pure titanium anode cannot be successfully used as a sacrificial anode because of the dielectric oxide layer which forms on its surface unless a quite high voltage is applied to it. In U.S. Patent No. 3,033,775 a titanium alloy is used with such elements as cobalt, nickel, manganese, zinc, tin or the like to effect a lowering of a polarization potential of titanium thereby making it a good sacrificial anode. Indeed it has long been recognized that pure titanium does not perform satisfactorily as a soluble or sacrificial anode material because of the electrically resistance oxide film that forms on its surface.

A final problem faced by those desiring to develop a successful antifouling system is hydrogen embrittlement of the ship's hull. When electrolytic action takes place close to the surface of the ship's hull, such as in some of those systems described above, hydrolysis of the sea water may occur. Such hydrolysis releases hydrogen ions which cause embrittlement of the ship's hull. Consequently it is important in any antifouling system which is installed that the system not be operated at such high currents to cause hydrolysis of the water thereby releasing hydrogen. This problem has prevented others in the art from developing a high voltage antifouling device which can successfully prevent the adherence of marine organisms without causing hydrogen embrittlement.

According to the present invention, there is provided an article having a conductive surface intended to be immersed in brackish or sea water, the article being provided with a potentiometric antifouling device for preventing adherence of marine organisms to the conductive surface when the surface is immersed in brackish or sea water and for simultaneously preventing corrosion of the conductive surface when the surface is immersed in brackish or sea water, the potentiometric antifouling device comprising at least one titanium electrode for immersion in said brackish or sea water, a dielectric oxide layer electrically formed on and completely covering said titanium electrode for limiting current flow to said conductive surface, means insulatively mounting said titanium electrode adjacent to and spaced from said conductive surface.

and means connected to said titanium electrode and said conductive surface for providing a voltage potential therebetween causing current flow from the surface of said titanium electrode to said conductive surface.

The present invention also provides a method of preventing adherence of marine organisms to a conductive surface which is spaced from a titanium anode immersed in brackish or sea water, which method comprises applying a voltage potential between said titanium anode and said conductive surface, forming a dielectric oxide layer under the influence of said potential on said titanium anode, and causing limited current flow to said conductive surface from said titanium anode through said oxide.

The present invention inhibits fouling of a submerged object such as a ship's hull by barnacles and other marine organisms and also inhibits corrosion of the object. A high voltage potential is applied between a titanium anode and the hull of the ship permitting only a small current flow from the hull of the ship through the sea water to the titanium electrode. When the voltage potential is initially impressed, an oxide layer is electrically formed on the titanium electrode which acts as a dielectric layer limiting current flow to the anode. Because of the dielectric effect of the oxide layer, even when high voltages are applied to the system, only limited current flows through the sea water and hydrolysis does not occur. The high voltage potential applied between the titanium electrode and the hull of the ship and the current density on the hull of the ship which is in the range of 25 to 250 milliamps per square foot effectively prevent adherence of marine organisms to the hull's surface as well as prevent corrosion through cathodic protection. A bimetallic electrode of titanium with a conductive metal selected from the group of gold, silver, platinum and stainless steel can be used in an alternative embodiment. Also the surface portion of the object which is submerged in brackish or sea water may be overlayed with an inorganic, zinc-rich coating from which zinc ions diffuse into the water adjacent the hull. The coating can also contain copper powder to improve its antifouling characteristics particularly when the negative potential is removed.

For a better understanding of the invention, reference will now be made, by way of example, to the accompanying drawings in which:

Fig. 1 is a cross-section representation of the hull of a ship provided with an antifouling and anticorrosion device;

Fig. 2 is an electrical circuit diagram, electrically equivalent to the arrangement shown in Fig. 1;

Fig. 3 is a representation of a preferred installation of the anodic electrode on the hull of a ship;

Fig. 4 is a perspective view of an alternative electrode;

Fig. 5A is a cross-section representation of a submerged object provided with an antifouling and anticorrosion device; and

Fig. 5B is a detailed cross-section representation of a portion of Fig. 5A.

Reference will now be made in detail to the present preferred embodiment of the invention, examples of which are illustrated in the accompanying drawings.

Referring first to Fig. 1 there is shown a cross-section of a ship's hull 10 on which a potentiometric antifouling device is mounted. The hull 10 is submerged in sea water or brackish water 12 to the water line 14.

In the present invention marine organisms are prevented from adhering to the conductive surface 16 of the hull 10, which surface is often metallic, by impressing a high voltage between the hull 10 and electrode 18. If the hull is made of wood, fiberglass or some other non-metallic material, a conductive paint or coating applied to the submerged surface is required in order for the anti-fouling device to operate effectively. The present invention, by impressed-current cathodic action, also prevents corrosion at the surface 16.

At least one titanium electrode 18 is mounted next adjacent to and spaced from the conductive surface 16. One or more titanium electrodes 18 are mounted below the water line 14 and spaced from the surface of hull 10 and extend from bow to stern of the shop (See Fig. 3). Other configurations of the electrodes on the hull 10 will also be obvious to one in the art dependent on the size and shape of the surface area to be protected from fouling.

As here shown means are provided for insulatively mounting the electrode 18, for adding structural strength to the system and for establishing an insulated electrical conduit through the hull 10 for connection to the power supply 20.

As here shown the means for insulatively mounting the electrode includes a gland body 22 which penetrates the hull 10 in a water tight manner and a hanger element 24, connected to the gland body and projecting outwardly from the hull 10. The gland body 22 and the hanger element 24 provide an internal conduit for a conductive element 26. These elements are insulated, by means well known in the art, to prevent short circuiting to the hull 10. The conductive element 26 is electrically connected with the titanium electrode 18. A fastener 28 such as a nut holds the electrode 18 against the hanger element 24.

Means 20 are connected to the titanium electrode 18 and the conductive surface 16 of the hull 10 for providing a voltage potential therebetween. Preferably the means 20 is a d.c. power supply or battery. The positive terminal of the battery is connected through a variable resistance 30 to the electrode 18 which functions as an anode. A connection from the negative terminal of battery 20 is made to point 32 of a conductive portion of hull 10. When the submerged surface area of the hull is large, additional contacts from the negative terminal of battery 20 to spaced apart points on the hull may be required to assure a proper potential gradient across the entire surface.

A dielectric oxide layer 34 is electrically formed to completely cover the titanium electrode 18 for limiting current flow from the conductive surface 16. The oxide film 34 is developed by applying a positive voltage with respect to the conductive surface 16 to the anode 18. Current flows through the sea water, which functions as an electrolyte, for a short period until the oxide film begins to build up on the titanium anode 18. Subsequently, because of the dielectric effect of the film, the current will diminish. The oxide layer will ultimately form to a thickness of approximately 200 angstroms.

It is known that aluminum and magnesium also will form an oxide film in a manner similar to titanium. However, such oxide films are much thinner and consequently fail to operate as effectively to limit current. The oxide layer formed on titanium is impermeable to the sea water as well as being self healing, should it be scratched or physically removed.

Referring now to Fig. 2, there is shown a simplified equivalent electrical circuit of the arrangement of Fig. 1. The center line 36 schematically represents the water line on the hull of the ship.

The power supply, here represented as battery 20, is connected to anode 38 which is equivalent to the electrode 18 of Fig. 1. A variable resistance 30 is connected between the anode 38 and the positive terminal of battery 20 for control of current in the circuit. The voltage potential on the hull as a consequence will be more negative with respect to the battery reference voltage than if the resistance 30 is placed between the negative terminal of battery 20 and the conductive surface 16 of hull 10. Better antifouling results are obtained when the cathodic plate, i.e. the surface 16, is made more negative. The negative terminal of battery 20 is connected to the hull of the ship at point 32. The equivalent electrical circuit between the anode 18, the dielectric layer 34, the sea water 12 and the conductive surface 16 of hull 10 is represented in Fig. 2 as the parallel circuit comprised of resistance 40 and capacitor 42.

Because of the dielectric effect of the thick oxide layer 34 a relatively high voltage can be applied between points 38 and 32 permitting only a small current through resistance 40, i.e. through sea water 12. Consequently a current density in the conductive surface 16 can be maintained at a level between 25 and 250 milliamperes per square foot when a voltage in the range of 2 to 10 volts is applied between points 38 and 32. This prevents the adherence of marine organisms but does not cause hydrolysis of the sea water with the accompanying bad effects of hydrogen embrittlement of the hull structure.

If a bimetallic electrode is used as an anode, as depicted in Fig. 4, a voltage greater than 10 volts at the same or greater amperage can be applied between the anode 18 and the conductive surface 16 without breakdown of the oxide film. In Fig. 4 there is shown a bimetallic electrode 44 composed of titanium 46 and another conductive metal 48 selected from the group of platinum, silver, gold, stainless steel or other non-soluable conductive metals. The conductive metal can be plated on the titanium or otherwise combined with the titanium to effect a good electrical contact between metals.

The purpose of the other conductive metal is to allow increased potentials to be applied to the anode at the same or greater amperage levels without destruction of the oxide layer 34. The surface area of the conductive metal must, however, be limited in proportion to the amount of current flow desired. The conductive metal provides an alternative region for current flow and effectively protects breakdown of the oxide layer 34. It has been found that the potentiometric antifouling device operates effectively with such a bimetallic anode to levels of 50 volts. Further it is believed that the higher voltage levels permit a better and more uniform potential distribution across the surface of the hull, thereby providing better antifouling results as well as anti-corrosion effects over a wider area of the hull for a given sized anode structure.

Referring now to Fig. 3 there is shown one installation of the titanium anode which is effective for preventing adherence of marine organisms across a wide area of the hull's surface 16. A preferred structure is for the elongated electrode 18 to extend parallel with the keel 50 of the ship extending from bow to stern of the ship 52. An elongated electrode can be mounted on each side of the hull.

For purposes of providing a better understanding of the invention, the following illustrative examples are given:

Example I

The hull of a 28-foot long galvanized life boat was used as a cathode in an arrangement similar to that shown in Fig. 1. Elongated titanium electrodes, two inches wide and one-quarter inch thick, were mounted on the hull below the water line. One such electrode was mounted on either side of the hull extending from bow to stern. The electrodes were mounted upon rubber insulators and spaced approximately 3 inches from the hull. A voltage of nine volts d.c. at 250 milliamperes was applied to the system. After three weeks, the wooden rudder of the boat had become heavily fouled with marine organisms, but there was no evidence of fouling on the hull other than a film of detritus only at the water line. Fouling was greatly inhibited.

At the end of nine weeks, there was evidence of heavy fouling on the wooden rudder, while the hull showed evidence of fouling only on some surface areas, proportional to the distribution of potential.

Example II

A five gallon drum was placed in sea water and the submerged conductive surface thereof was connected as the cathode in an arrangement similar to that shown in Fig. 1. Thin, elongated, and perforated titanium electrodes, 18 inches by 1 inch, were mounted on either side of the drum below the water line. The electrodes were spaced 2 inches from the drum surface. A current limiting resistance of 300 ohms was inserted between the positive terminal of the battery and the titanium electrodes. A 36 volt potential was applied to the system. The current density on the conductive surface of the drum was measured at 25 milliamperes per square foot. Over a period of three weeks no significant fouling was observed.

Example III

The apparatus described in Example II above was modified by attaching stainless steel rods to the titanium anodes. The applied voltage was then raised to 48 volts, providing sufficient current density on the conductive surface of the drum to prevent corrosion. The current density was 60 milliamperes per square foot. Over a period of six weeks no fouling or corrosion was observed.

Referring to Fig. 5A, there is shown a cross-section of a submerged object, shown here as a ship's hull 10, on which a potentiometric antifouling and anticorrosion device is mounted. The hull 10 is submerged in sea water or brackish water 12 to the waterline 14.

In accordance with the present embodiment, surface portion 16 of hull 10 is overlaid by an inorganic zinc-rich coating 54. Preferably coating 54 is comprised of 80-90% zinc powder by dry film weight, 5-10% copper powder by dry film weight and the remainder, a suitable binding material.

The inorganic zinc-rich coating preferably has a silica base such as sodium or potassium silicate. Such a coating forms a very smooth, glass-like coating, having zinc and copper powder locked closely to the hull by the silica. The coating is very tough and withstands abrasion and impact which ordinarily would penetrate other types of paint films. Further, the zinc-rich paint coating is conductive of electricity because of the large amount of zinc it contains. The silicate binder almost totally prevents "chalking" or abrasion, thus giving a long life to the coating. It is however preferred that such coating is so arranged and composed that zinc and copper ions will diffuse into the water at the interface of the water and the coating.

The embodiment shown in Fig. 5A is otherwise the same as that shown in Fig. 1.

It is assumed that hull 10 is conductive and that coating 54 will therefore be at the same negative potential as hull 10. It will be understood that if hull is not conductive, a connection can be made through the hull to the conductive coating 54.

Referring now to Fig. 5B, there is shown a detailed cross-section of hull 10 shown in Fig. 5A. As embodied herein, zinc-rich coating 54 is applied to a portion of surface 16 of hull 10. Coating 54 also preferably includes in addition to zinc powder, a copper powder.

In accordance with the present invention, when a negatative potential is applied to hull 10 which is submerged in brackish or sea water 12, it is possible to prevent corrosion and fouling for extended periods of time. Since most marine organisms at the microscopic level are negative in charge, the negatively charged hull tends to repel such organisms. However, the metal ions, zinc and copper, which go into solution at the interface between the coating 54 and the water 12 are positve. Consequently, the positive ions 60 are attracted toward the hull 10 and held in a layer adjacent coating 54.

If a low potential area develops on the hull as shown in Fig. 5B at 62, or should the negative potential be removed from the hull, the zinc-rich coating will still protect hull 10 from corrosion while positive copper ions will immediately diffuse into water 12 to poison nearby marine organisms. A diffusion of positive ions 60 thus will form at the coating water interface.

When the negative potential is again applied, positive metal ions will be held closely to the negatively charged hull 10 in a tight electrostatic layer and will not be allowed to diffuse away from the coating water interface as normally occurs with conventional antifouling paints. Because the

negatively charged hull 10 prevents diffusion of the layer of positive metal ions which are poisonous to the marine organisms and simultaneously repels marine organisms from hull 10, the system performs as an effective antifouling and anticorrosion device with a potential life well beyond that of conventional systems which use antifouling coatings alone.

In accordance with the present invention, the device utilizes an inorganic zinc-rich coating that is superior in life and quality to most other such coatings and which when a negative potential is applied thereto also provides superior antifouling characteristics.

The inorganic zinc-rich coating is preferred in that it does not tend to blister with high impressed current nor does it readily dissolve thereby reducing its lifetime. Aluminum and magnesium powders also are corrosion-preventing pigments, but because their oxides are highly soluble, are not as suitable as the zinc-rich coating.

WHAT WE CLAIM IS:-

1. An article having a conductive surface intended to be immersed in brackish or sea water, the article being provided with potentiometric antifouling device for preventing adherence of marine organisms to the conductive surface when the surface is immersed in brackish or sea water and for simultaneously preventing corrosion of the conductive surface when the surface is immersed in brackish or sea water, the potentiometric antifouling device comprising at least one titanium electrode for immersion in said brackish or sea water, a dielectric oxide layer electrically formed on and completely covering said titanium electrode for limiting current flow to said conductive surface, means insulatively mounting said titanium electrode adjacent to and spaced from said conductive surface, and means connected to said titanium electrode and said conductive surface for providing a voltage potential therebetween causing current flow from the surface of said titanium electrode to said conductive surface.

2. An article as claimed in claim 1, wherein said titanium electrode includes a second metal in electrical contact with the titanium.

3. An article as claimed in claim 2, wherein said second metal is platinum, stainless steel, gold or silver.

4. An article as claimed in any of claims 1 to 3, wherein said means for providing a voltage potential between said titanium electrode and said conductive surface is capable of applying a voltage potential of nine volts or more and of producing a current density of from 25 to 250 milliamps per square foot at said conductive surface.

5. An article as claimed in any of claims 1 to 4, wherein said means for providing a voltage potential between said titanium electrode and said conductive surface is a battery.

6. An article as claimed in claim 5, wherein the negative terminal of said battery is connected to a plurality of spaced apart points on said conductive surface.

7. An article as claimed in claim 5 or 6, wherein a current limiting resistance is connected between the positive terminal of said battery and said titanium electrode.

8. An article as claimed in any of claims 1 to 7, wherein said titanium electrode is mounted by means of (a) a gland body penetrating said conductive surface in a water-tight manner, (b) a hanger element extending from said gland body for mounting said titanium electrode, and (c) a conductive element carried in an insulative manner by said gland body and said hanger element and electrically connected to said titanium electrode.

9. An article as claimed in any of claims 1 to 8, wherein said conductive surface is metallic.

10. An article as claimed in any of claims 1 to 8, wherein said conductive surface is the surface of a conductive paint or coating.

11. An article as claimed in claim 10, wherein said conductive coating is an inorganic zinc-rich coating of a structure and composition such that, when the coating is immersed in brackish or sea water, zinc ions diffuse into the water at the interface of the water and the coating.

12. An article as claimed in claim 11, wherein said inorganic zinc-rich coating contains copper powder.

13. An article as claimed in claim 11 or 12, wherein said inorganic zinc-rich coating comprises sodium silicate enriched with zinc.

14. An article as claimed in claim 11 or 12, wherein said inorganic zinc-rich coating comprises potassium silicate enriched with zinc.

15. An article as claimed in any of claims 1 to 14, the article being a ship's hull.

16. A ship's hull as claimed in claim 15, substantially as hereinbefore described with reference to, and as shown in, the accompanying drawings.

17. A method of preventing adherence of marine organisms to a conductive surface which is spaced from a titanium anode immersed in brackish or sea water, which method comprises applying a voltage potential between said titanium anode and said conductive surface, forming a dielectric oxide layer under the influence of said potential on said titanium anode, and causing limited current flow to said conductive

surface from said titanium anode through said oxide.

18. A method according to claim 17, wherein a voltage potential above nine volts is applied between said titanium electrode and said conductive surface, and wherein a current density between 25 and 250 milliamperes per square foot is developed on said conductive surface.

19. A method according to claim 17 or 18, wherein said titanium electrode includes a second metal in electrical contact with the titanium.

20. A method according to claim 17, substantially as hereinbefore described with reference to the accompanying drawings.

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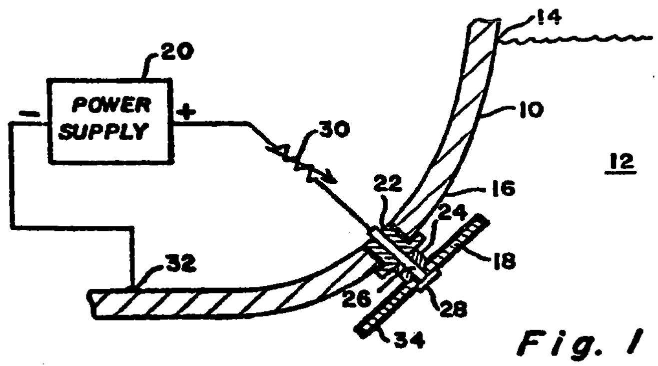
Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1981. Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.


14
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POWER SUPPLY
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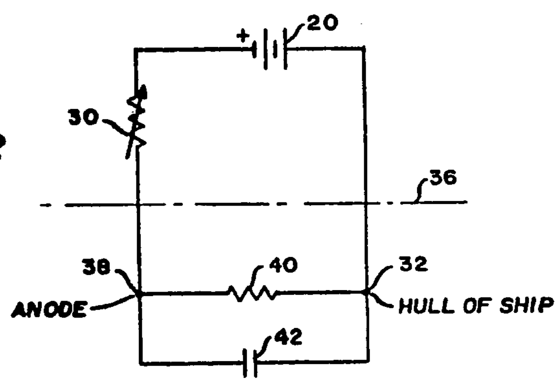
Fig. 1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36
38
40
32
ANODE
HULL OF SHIP
42

Fig. 2

1597305 COMPLETE SPECIFICATION

3 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 2

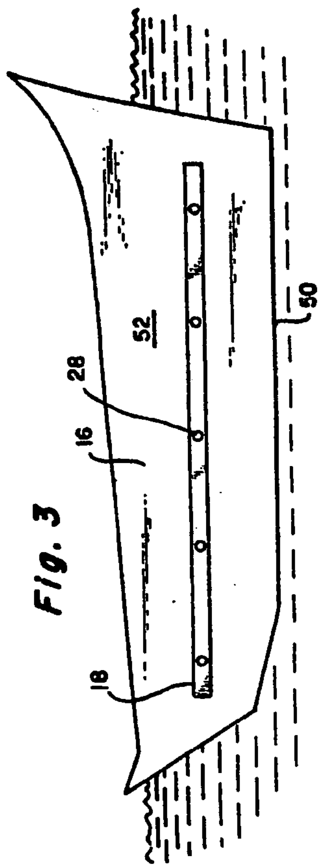

Fig. 3

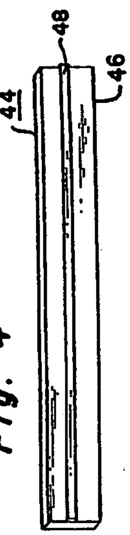

Fig. 4

1597305 COMPLETE SPECIFICATION

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Sheet 3

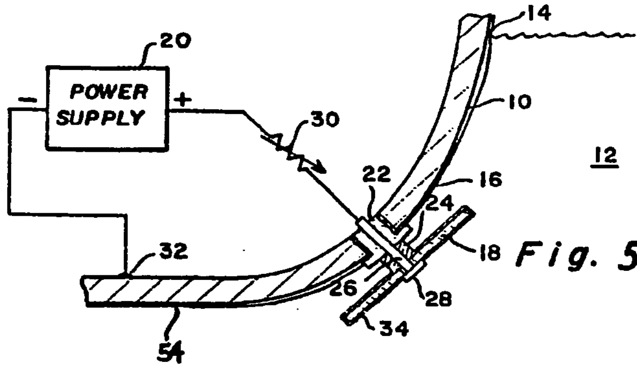

Fig. 5A

Fig. 5B